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Hydrothermal and Cold Spring Water and Primary Productivity Effects on Magnesium Isotopes: Lake Myvatn, Iceland

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Lake Myvatn, Iceland, is one of the most biologically productive lakes in the northern hemisphere, despite seasonal ice cover. Hydrothermal and groundwater springs make up the dominant source to this lake, and we investigate their Mg isotope ratio to assess the effect of mid-ocean ridge hydrothermal springs, which are the primary modern sink of seawater magnesium. We also examine a time series in the only outflow from this lake, the Laxa River, to assess the effects of seasonal primary productivity on Mg isotopes. In the hydrothermal waters, there is a clear distinction between cold waters (largely unfractionated from primary basalt) and relatively hot waters, which exhibit over 1‰ fractionation, with consequences for the oceanic mass balance if the hydrothermal removal of Mg is not fully quantitative. The outflow Mg isotopes are similar to basalts ($\delta^{26}\text{Mg} = -0.2$ to -0.3) during winter but reach a peak of ~ 0 ‰ in August. This fractionation corresponds to calcite precipitation during summer in Lake Myvatn, preferentially taking up light Mg isotopes and driving the residual waters isotopically heavy as observed, meaning that overall the lake is a CO_2 sink.

Keywords: weathering (IGC: D3/D5/D6), isotope geochemistry, carbonate chemistry, hydrothermal spring, groundwater (G.W.), phytoplankton

INTRODUCTION

Chemical weathering of continental silicate rocks is the primary long-term drawdown process of atmospheric CO_2 (Walker et al., 1981; Berner et al., 1983; Chamberlin, 1899). Dissolution of Ca–Mg silicates dissolves CO_2 , transports it to the oceans as bicarbonate via rivers, where it, and Ca and Mg, is sequestered into marine carbonates (Berner, 2003). Continental weathering also provides many critical nutrients to the coastal oceans (e.g., Fe, P), which fertilize organic carbon growth (Gíslason et al., 2006). Finally, continental weathering and erosion processes deliver particulate clays and reactive iron to the oceans, which enhance organic carbon burial (Kennedy and Wagner, 2011; Lalonde et al., 2012; Kennedy et al., 2014; Hawley et al., 2017). In short, weathering controls the climate both on short timescales (via organic carbon growth and burial) and long timescales

(via carbonate precipitation). Chemical weathering also affects the carbonate saturation state of the oceans on millennial timescales, affecting its pH and ability to store CO₂ (Archer et al., 2000).

However, there are a number of still open questions on these processes, including the ultimate controlling mechanism of silicate weathering [where both climate (via temperature and runoff) and supply of fresh primary silicates are likely important (Raymo and Ruddiman, 1992; West et al., 2005)], and the rate at which any weathering-related feedback can mitigate climate change. One reason why these questions have not been resolved is that no truly unambiguous tracers of weathering, both in the present and in the geological record, have been determined. For example, traditional radiogenic isotopes (e.g., ⁸⁷Sr/⁸⁶Sr or ¹⁸⁸Os/¹⁸⁷Os) have been used to quantify palaeo-weathering (Peucker-Ehrenbrink et al., 1995; McArthur et al., 2001; Bickle et al., 2005). However, they suffer from a strong lithological control (i.e., the isotope ratio of rivers is controlled by the isotope ratio of rocks being weathered) and often cannot distinguish between weathering of silicates and carbonates (Palmer and Edmond, 1992; Oliver et al., 2003). For this reason, other isotopic tracers have been sought, often from the “non-traditional” stable metal isotopes. In this study, we not only focus on magnesium isotopes but also compare them to silicon and lithium isotopes previously measured in the same samples.

Magnesium is of interest because it is an element directly involved in the long-term carbon cycle. It is weathered from rocks on the continents and then sequestered in the oceans into carbonates (primarily dolomites and high-Mg calcites), as well as substituting for Ca in hydrothermal interactions with basalt at mid-ocean ridges. The reactions that control this process largely involve greenschist-facies metamorphism of oceanic basalts, where Mg is basically lost into high-temperature secondary minerals, such as olivine reacting to chlorite or plagioclase reacting to albite + epidote (Humphris and Thompson, 1978; Berner et al., 1983; Albarede and Michard, 1986; Elderfield and Schultz, 1996; Gaillardet et al., 1999; Holland, 2005; Tipper et al., 2006b; Higgins and Schrag, 2015). Hence, weathering is the primary source of Mg to the oceans, while the two main sinks are carbonates and hydrothermal fluids, with additional minor sinks during low-temperature clay formation (Tipper et al., 2006b).

Magnesium has three stable isotopes (²⁴Mg, ²⁵Mg, and ²⁶Mg), with isotope ratios reported as δ²⁶Mg, which is the deviation of the 26/24 ratio from the standard DSM-3 (Galy et al., 2003). Simple dissolution imparts no Mg isotope fractionation (Wimpenny et al., 2010, 2014). During continental weathering, Mg isotopes in surface waters are strongly controlled by the dissolution mixing of isotopically light carbonates and heavy silicates (Tipper et al., 2006a, 2008; Brenot et al., 2008; Wombacher et al., 2011; Pogge von Strandmann et al., 2019b,c). Furthermore, there is additional isotopic fractionation during the formation of secondary minerals from silicate weathering, where these minerals tend to prefer the heavy Mg isotopes (Tipper et al., 2006a,b, 2008, 2010, 2012a; Pogge von Strandmann et al., 2008; Chapela Lara et al., 2017; Hindshaw et al., 2020). The same direction of fractionation occurs during Mg sorption onto mineral surfaces (Huang et al., 2012; Opfergelt et al., 2012, 2014;

Pogge von Strandmann et al., 2012). Finally, the uptake of Mg by plants causes variable isotope fractionation (Black et al., 2006; Ra and Kitagawa, 2007; Bolou-Bi et al., 2012).

While a considerable body of literatures exists on Mg isotope behavior in rivers and occasionally groundwaters, much less is known about Mg isotope fractionation in continental hydrothermal fluids (Tipper et al., 2006b; Huang et al., 2018; Oelkers et al., 2019; Pogge von Strandmann et al., 2019c). This is potentially also important for the removal of Mg from seawater. While it has been generally considered that the hydrothermal removal of Mg is quantitative (and hence causes no isotope fractionation) (Holland, 2005; Higgins and Schrag, 2015), totally quantitative reactions are rarely observed in geochemistry and hence raises the interesting possibility of considerable isotope fractionation occurring. Equally, little is known about Mg isotope fractionation during uptake by phytoplankton, important for the budgets of all surface waters.

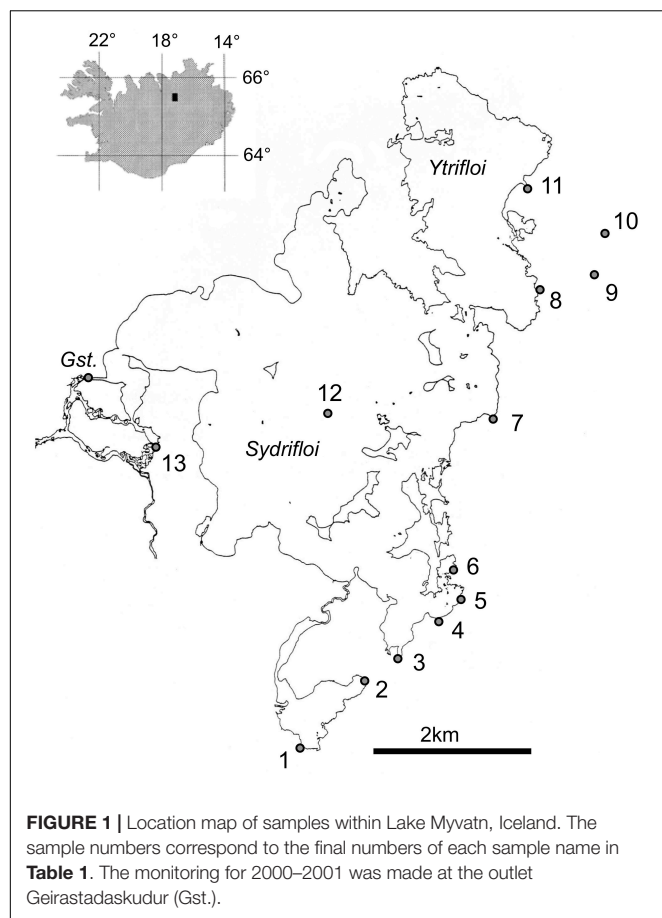
In this study, we present Mg isotope data from high- and low-temperature groundwaters that dominantly source Lake Myvatn, Iceland. The high-temperature, hydrothermal, waters have undergone water–rock interactions at temperatures up to ~300°C (cooled during transport to 17–44°C), while the cold groundwaters are at temperatures of 3–7°C. These samples allow the comparison of the effect of temperature on groundwaters from the same area, and particularly the impact on Mg isotope behavior. We also report Mg isotope data from a time series from the single outflow from Lake Myvatn, the Laxa River. The lake has significant seasonal changes in primary productivity that strongly affect its water chemistry and provides an opportunity to study the effects of phytoplankton (including a large component of diatoms) on isotope fractionation.

Field Area

Lake Myvatn (65°35' N, 17°00' W) is a shallow eutrophic lake in the northeast of Iceland located close to the Arctic Circle (**Figure 1**). The lake's altitude is 278 m above sea level, and it has a maximum depth of ~4.2 m, with an area of ~37 km². During the summer (ice-free) season (mid-May to late-September), the entire water column is well-mixed. The primary water sources to the lake are groundwaters, with the southern basin (Sydrifloi) fed by cold springs, and the northern basin (Ytrifloi) fed by hot springs (Pogge von Strandmann et al., 2016). The heat in the hot springs stems from the Namafjall and Krafla geothermal fields (Kristmannsdottir and Armannsson, 2004). Only one river (the Laxa River) drains the lake, and the water in the lake has a residence time of about 27 days (Olafsson, 1979a).

The underlying geology of the lake is basaltic and ~2,300 years old, formed by a major basaltic volcanic eruption. Since then, the local geology has been modified by more recent eruptions, including the Krafla Volcano's 1725–1729 and 1975–1984 eruptions (Thordarson and Hoskuldsson, 2002; Hauptfleisch and Einarsson, 2012).

Despite winter ice cover, the lake is one of the most biologically productive in the northern hemisphere. This is due to high nutrient delivery from the groundwater sources, causing very high seasonal productivity, mainly associated with diatoms, green algae, and cyanobacteria (Olafsson, 1979b; Gislason et al., 2004;



Thorbergdottir and Gislason, 2004; Opfergelt et al., 2011). Biological activity in the lake also controls the concentrations of many dissolved metals. When the lake is covered by ice, sediment pore waters become enriched in nutrients relative to the lake waters by several orders of magnitude. These nutrients are then subsequently released by bioturbation, as well as sediment resuspension and diffusion, in the ice-free summer, leading to high nutrient fluxes and hence primary productivity (Gislason et al., 2004).

Samples were taken from both the “cold” and “hot” springs sourcing the lake in August 2009, and a monthly time series spanning March 2000 to March 2001 was taken from the Laxa River draining the lake following sampling protocols outlined in Opfergelt et al. (2011).

MATERIALS AND METHODS

Major and trace element concentrations were measured by Opfergelt et al. (2011) and were determined by inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography. At each site, pH and temperature were measured *in situ* (Opfergelt et al., 2011). For Mg isotope analysis, sufficient water was dried down to attain $\sim 1 \mu\text{g}$ of Mg. This was passed through a two-step cation exchange chromatography

procedure, using AG50W X-12 resin, and using 2 M HNO_3 as an eluent. Isotopic analyses were conducted on a Thermo Neptune multicollector ICP-MS at the Bristol Isotope Group, normalizing to the standard DSM-3.

This procedure has been described in detail before (Pogge von Strandmann et al., 2011), and resulting standards have been shown in multiple compilations and interlaboratory comparisons (Foster et al., 2010; Pogge von Strandmann et al., 2011; Teng et al., 2015; Shalev et al., 2018). During the analyses of this study's waters, seawater was used as a standard, with a $\delta^{26}\text{Mg} = -0.82 \pm 0.05\text{‰}$ ($n = 3$), which agrees with the long-term running average of over 10 years (Foster et al., 2010) and where $\delta^{26}\text{Mg} = ({}^{26}\text{Mg}/{}^{24}\text{Mg}_{\text{sample}}/{}^{26}\text{Mg}/{}^{24}\text{Mg}_{\text{DSM-3}} - 1) \times 1,000$.

The solution elemental concentrations were used to calculate mineral saturation states using PHREEQC and a combination of its standard thermodynamic database, plus THERMOCALC and MINTED databases (Parkhurst and Appelo, 1999). These are reported as the logarithmic saturation index, SI, where positive numbers indicate supersaturation, and negative numbers indicate undersaturation.

RESULTS

Hydrothermal and Cold Groundwaters

All results are listed in **Table 1**, and the sample locations are shown in **Figure 1**. The groundwaters that are the primary source to Lake Myvatn are undersaturated with respect to the primary basaltic minerals of glass, olivine, pyroxene and plagioclase, as well as minerals such as calcite. Secondary minerals such as kaolinite are supersaturated, while smectites are supersaturated at relatively low pH (8–9) but undersaturated at higher pH. Secondary minerals that are known to remove Mg in seawater hydrothermal settings, such as chlorite or Mg-rich smectite (Haymon and Kastner, 1986), are also supersaturated.

Magnesium concentrations vary between 74 and 160 $\mu\text{mol/l}$, on average 50% or more lower than river waters from Iceland (Gislason et al., 1996). The “cold” groundwaters ($< 7.5^\circ\text{C}$) are on average slightly less concentrated than the “hot” groundwaters (106 vs. 126 $\mu\text{mol/L}$, respectively).

Mg isotope ratios ($\delta^{26}\text{Mg}$) vary between -1.36 and -0.16‰ , with the cold waters being on average significantly isotopically heavier (average, -0.40‰) compared to the hot groundwaters (-1.01‰). Overall, the Mg isotope ratios negatively covary with elemental concentrations such as Na, and overlap with, but extend to lower values than Icelandic river waters (Pogge von Strandmann et al., 2008). There is no evidence of mixing between different Mg sources (e.g., seawater via precipitation) in any of the samples (**Figure 2**).

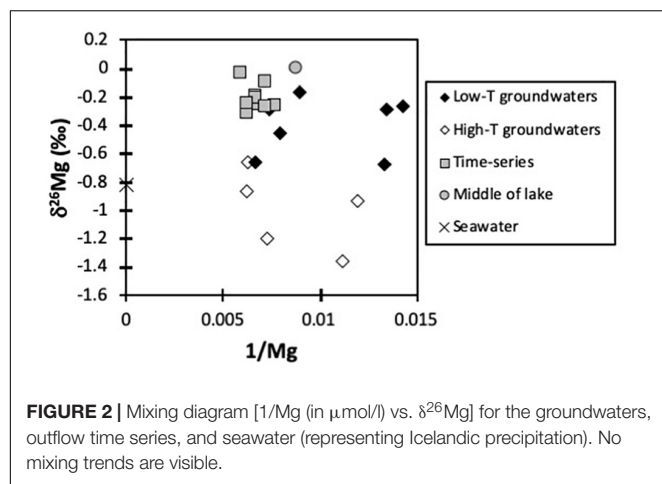
Laxa River Outflow

The Mg concentration of the outflow time series is overall slightly higher than most of the groundwater springs, with values ranging from 130 to 170 $\mu\text{mol/L}$. There is no obvious seasonal trend, although the highest concentrations are in the summer. Mg isotope ratios, in contrast, are strongly seasonal, with $\delta^{26}\text{Mg}$ values of -0.31 to -0.24‰ in the winter (ice-covered) months,

TABLE 1 | Concentration and isotope data for the Lake Myvatn samples.

Sample	Sample month	Temperature	pH	Conductivity	Na	K	Mg	Ca	Al	Si	P	Ti	NO ₃	$\delta^{25}\text{Mg}$ (‰)	2se	$\delta^{26}\text{Mg}$ (‰)	2se	$\Delta^{25}\text{Mg}$ (‰)
		°C		$\mu\text{ S/cm}$	mM	mM	mM	mM	μM	mM	μM	μM	μM					
Input springs																		
IC/MY/01.09		3.4	9.27		0.53	0.02	0.07	0.11	0.45	0.29	1.41	0.017		−0.15	0.02	−0.29	0.02	0.00
IC/MY/02.09		7	9.4	130	0.72	0.03	0.11	0.12	0.53	0.31	1.5	0.018		−0.09	0.02	−0.16	0.03	−0.01
IC/MY/03.09		6.5	9.21	141	0.67	0.03	0.15	0.15	0.5	0.3	1.6	0.019		−0.33	0.00	−0.66	0.03	0.02
IC/MY/04.09		6.2	9.23	129	0.64	0.03	0.14	0.14	0.45	0.3	1.78	0.018		−0.17	0.01	−0.29	0.02	−0.02
IC/MY/05.09		5.8	9.6	115	0.74	0.02	0.07	0.11	0.67	0.31	1.83	0.019		−0.13	0.02	−0.26	0.01	0.00
IC/MY/06.09		7	9.6	134	0.81	0.02	0.08	0.11	0.59	0.34	1.58	0.019		−0.35	0.03	−0.68	0.02	0.01
IC/MY/07.09		7.5	9.29	156	0.9	0.03	0.13	0.16	0.48	0.35	1.72	0.02		−0.23	0.02	−0.46	0.00	0.01
IC/MY/08.09		16.5	8.68	359	2.02	0.1	0.16	0.3	0.62	1.38	0.92	0.035		−0.44	0.02	−0.86	0.03	0.01
IC/MY/09.09		37.3	8.29	505	3.32	0.15	0.08	0.35	1.06	2.25	0.58	0.042		−0.48	0.03	−0.94	0.01	0.01
IC/MY/10.09		44	8.1	437	2.64	0.15	0.09	0.28	0.2	2.23	0.51	0.038		−0.68	0.01	−1.36	0.03	0.02
IC/MY/11.09		24.3	8.29	396	1.73	0.1	0.16	0.51	0.32	1.2	0.82	0.026		−0.34	0.03	−0.66	0.03	0.01
IC/MY/14.09		20	3.5	620	2.55	0.27	0.14	0.2			0.69	0.142		−0.61	0.03	−1.20	0.04	0.01
IC/MY/12.09 -	Mid-lake	10.2	9.82	157	0.77	0.03	0.11	0.15	0.39	0.15	1.07	0.018		0.00	0.04	0.00	0.02	0.00
IC/MY/13.09 -	lake outflow	10.7	10	162	0.79	0.03	0.12	0.15	0.31	0.13	0.89	0.023		0.01	0.02	0.01	0.01	0.00
Laxa River																		
00A013	March-00	1.2	8.37		1.01	0.04	0.16	0.2	0.33	0.41			2.06	−0.15	0.01	−0.31	0.02	0.01
00A023	April-00	0	9.03		0.78	0.03	0.15	0.16	0.03	0.3			0.35	−0.15	0.03	−0.25	0.01	−0.02
00A031	May-00	6	8.52		0.75	0.03	0.13	0.15	0.3	0.22			0.15	−0.12	0.02	−0.26	0.03	0.01
00A044	June-00	12.3	9.63		0.88	0.03	0.15	0.18	0.4	0.1			0.98	−0.10	0.00	−0.19	0.01	0.00
00A053	July-00	15.7	9.93		0.95	0.03	0.14	0.18	1.08	0.05			1.01	−0.05	0.03	−0.09	0.02	0.00
00A062	August-00	15.5	9.78		1.04	0.04	0.17	0.2	0.49	0.09			0.17	−0.03	0.02	−0.03	0.02	−0.01
00A071	September-00	8.3	9.35		0.94	0.04	0.15	0.18	0.26	0.1			0.17	−0.14	0.03	−0.21	0.03	−0.03
00A080	October-00	1.4	8.73		0.95	0.04	0.16	0.18	0.15	0.16			0.15	−0.15	0.02	−0.29	0.01	0.00
00A089	November-00	0.6	8.32		0.97	0.04	0.16	0.19	0.18	0.31			0.51	−0.17	0.02	−0.31	0.03	−0.01
01A006	1-January	0.9	8.34		0.97	0.04	0.16	0.19	0.47	0.41			2.75	−0.12	0.03	−0.24	0.02	0.00
01A015	1-March	0.5	8.43		0.88	0.04	0.14	0.14	0.38	0.34			0.89	−0.12	0.04	−0.26	0.01	0.01

All parameters aside from Mg isotope ratios are repeated from Opfergelt et al. (2011). The $\Delta^{25}\text{Mg}$ represent the ‰ deviation from the terrestrial fractionation line.



increasing to a maximum of -0.03‰ in August, within the range of Icelandic river waters (Pogge von Strandmann et al., 2008). This yearly peak is similar to that observed for Al concentrations and inversely to Si concentrations, but not other nutrients like NO_3 , which exhibits two minima (Opfergelt et al., 2011).

Sample MY12 was collected from the middle of the Lake at the end of August 2009, and its $\delta^{26}\text{Mg}$ (0.00‰) is within analytical uncertainty of the outflow sample collected in August 2000 (-0.03‰), suggesting that the broad time series patterns observed in 2000–2001 are repeatable yearly cycles.

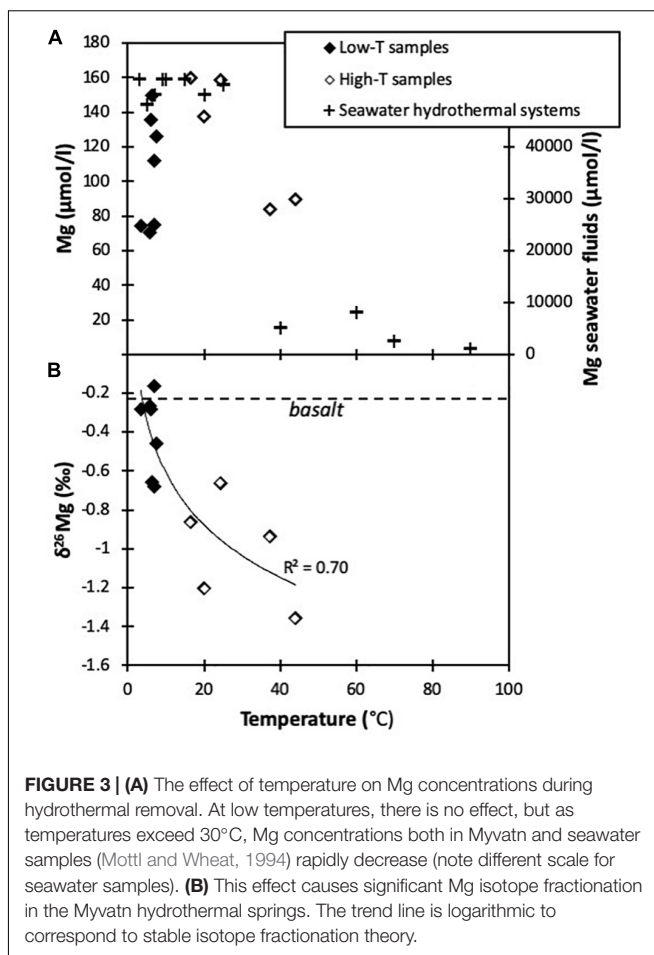
DISCUSSION

Hydrothermal and Cold Groundwaters

The primary modern sink of Mg from seawater is exchange of Mg for Ca during high-temperature basalt–water interactions (Holland, 2005). At the same time, the low-temperature alteration of the oceanic crust is likely to be at the very least a minor sink of Mg from seawater (Tipper et al., 2006b; Huang et al., 2018). The Myvatn groundwaters provide the opportunity to examine Mg isotope fractionation at various temperatures of basalt–water interaction.

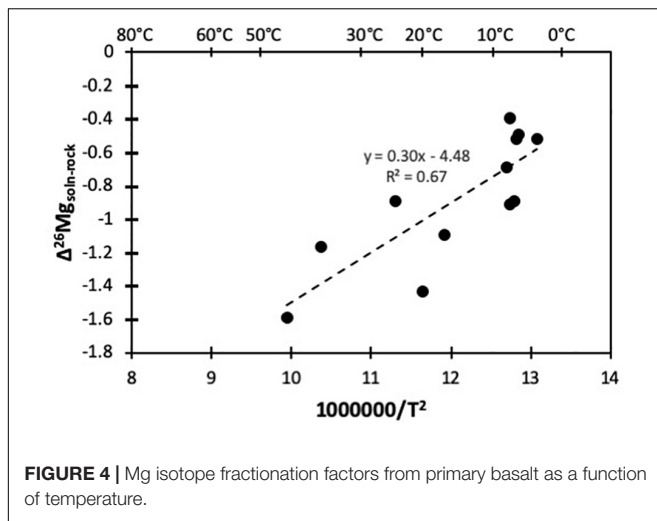
Mg concentrations in the low-temperature springs ($<7.5^\circ\text{C}$) are quite variable, ranging from 70 to $150 \mu\text{mol/L}$. However, the higher temperature springs show a negative covariation between [Mg] and temperature, such that the warmest samples have low [Mg] (Figure 3A). This is a broadly similar behavior to Mg concentrations during seawater–basalt interactions at mid-ocean ridges (Albarede and Michard, 1986; Mottl and Wheat, 1994; Elderfield and Schultz, 1996). There, [Mg] drops from concentrations of $> 90\%$ of that of seawater to $< 10\%$ of seawater once temperatures are $> 40^\circ\text{C}$. By 90°C , Mg concentrations are $< 2\%$ of that of seawater (Mottl and Wheat, 1994).

While overall concentrations are significantly lower in the Myvatn springs, because the original solution is not seawater, the overall relationship is similar and suggests that these results may be able to inform on Mg isotope fractionation occurring during Mg removal from seawater. It is therefore significant that



the Mg isotope ratios of these springs show a clear relationship with temperature (Figure 3B). The coldest groundwater ($\sim 3^\circ\text{C}$) has a $\delta^{26}\text{Mg}$ value that is indistinguishable from primary basalt [-0.29 vs. -0.23‰ , respectively (Pogge von Strandmann et al., 2008, 2011, 2012; Opfergelt et al., 2014)]. At slightly higher temperatures (> 3 , but $< 7.5^\circ\text{C}$), there is more fractionation ($\delta^{26}\text{Mg} = -0.68$ to -0.16‰), while at higher temperatures, Mg isotope ratios in the solution continue to decrease, reaching a value of -1.36‰ at 44°C . There are two general processes that could be causing greater Mg isotope fractionation at higher temperatures: (1) standard temperature-dependent stable isotope fractionation, which scales according to $1,000 \times \ln(\alpha)$ as a function of $10^6/T^2$ (where T is temperature in K, and $\alpha_{\text{rock/soln}}$ is the isotopic fractionation factor between solution and solid, which, for geological processes, approximates the $\Delta^7\text{Li}$ between two phases) (Faure, 1986); (2) removal of Mg into high-temperature secondary minerals, such as chlorite or smectite, which is the process by which most of the present-day Mg is removed from seawater (Humphris and Thompson, 1978).

Figure 4 shows that there is a covariation between the Mg isotope fractionation and temperature (shown as $1/T^2$), such that at higher temperature, the solution $\delta^{26}\text{Mg}$ is more fractionated from the basaltic starting composition. Such a relationship is, in effect, opposite from what would be expected from stable isotope



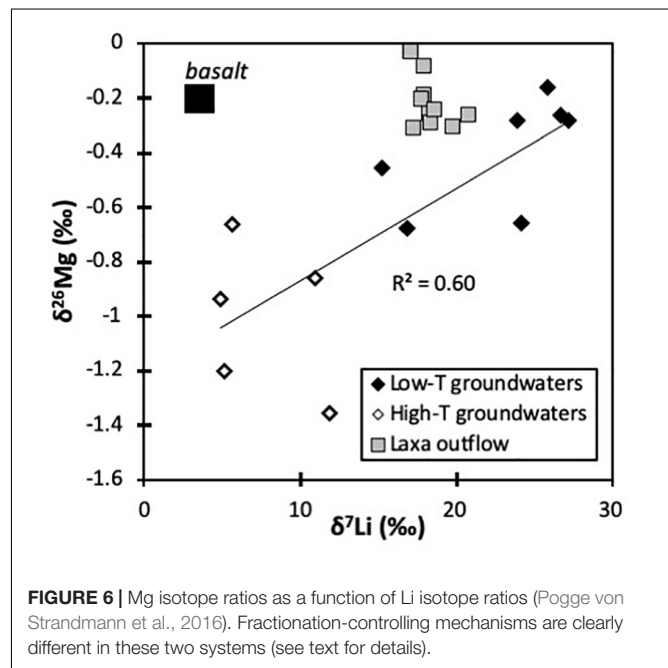
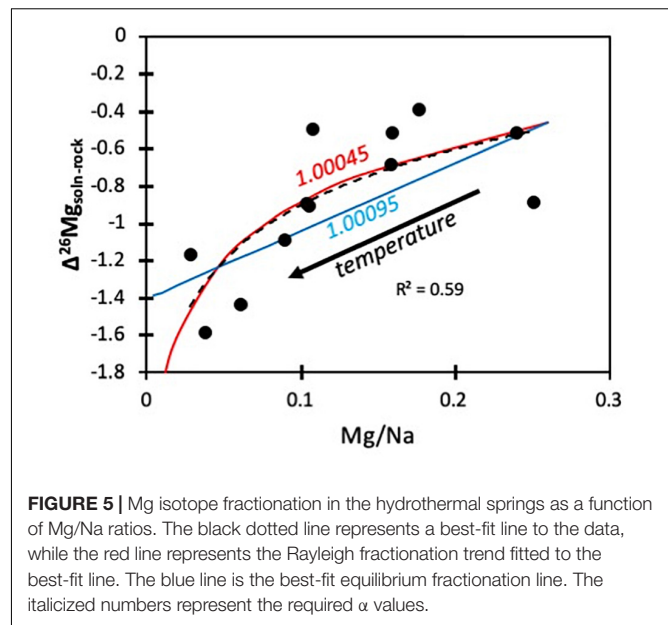
fractionation theory, where more fractionation occurs at lower temperature (Urey, 1947). It therefore seems likely that, while there is a temperature effect occurring, it is not dominantly due to simple stable isotope fractionation effects, suggesting that high-temperature secondary mineral formation may be playing a role.

In the case of basalt–seawater hydrothermal reactions, Mg is removed by high-temperature secondary mineral formation [such as chlorite (Berner et al., 1983; Albarede and Michard, 1986; Elderfield and Schultz, 1996; Gaillardet et al., 1999; Holland, 2005; Tipper et al., 2006b; Higgins and Schrag, 2015), which is supersaturated in these groundwaters]. The same effect can be observed by the negative covariation between $\Delta^{26}\text{Mg}$ and the Mg/Na ratio (Figure 5). As temperature increases, more Mg is removed, removing Mg preferentially over Na [which is the most soluble major cation in basalt weathering (Gislason et al., 1996)], and causing greater Mg isotope fractionation. The best-fit Rayleigh fractionation relationship requires an $\alpha_{\text{rock-solution}}$ (isotopic fractionation factor) value of 1.00045 (while for equilibrium fractionation, this would be 1.00095, although given the potential of Mg depletion during hydrothermal reactions, a Rayleigh relationship would be expected to be more accurate). The Rayleigh fractionation is given by:

$$\delta_f - \delta_i = 10^3 (f^{\alpha-1} - 1)$$

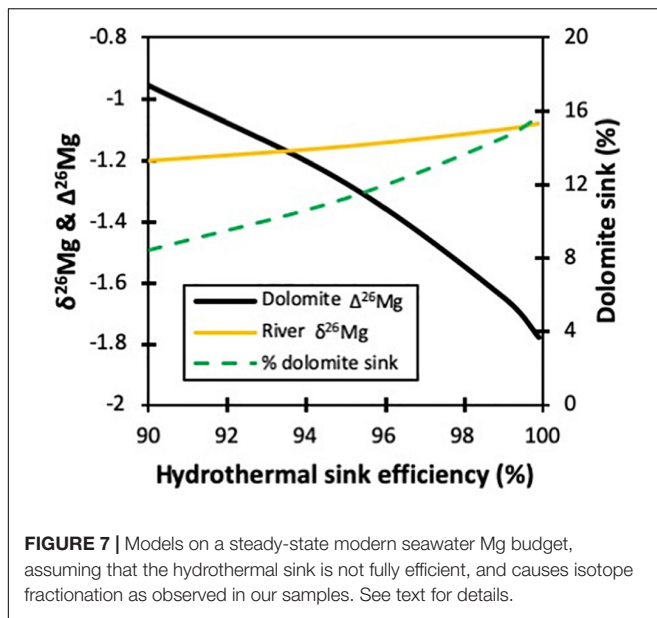
where δ_i is the isotope ratio (in delta notation) of the initial material, δ_f is that of the product, and f is the fraction of material remaining. Model estimates for the high-temperature hydrothermal removal of Mg have α values of 1.0000 (i.e., no isotopic fractionation) and values of 1.0007 for low-temperature clays (Higgins and Schrag, 2015). Experimental interactions between saponite (Mg-rich smectite) and seawater at 250 and 290°C report fractionation factors of 1.000345–1.000422 (Voigt et al., 2020), similar to our fractionation values.

The effect of hydrothermal fractionation on Mg isotopes can also be observed with a comparison to lithium isotopes. For Li, the low-temperature groundwaters are highly isotopically fractionated from the original basalt (Figure 6), while the high-temperature waters are relatively unfractionated. In effect, this



represents standard stable isotope fractionation behavior, plus the effect that, in hot waters, the secondary minerals that fractionate Li isotopes are more soluble and hence precipitate less (Pogge von Strandmann et al., 2017). The positive covariation between $\delta^7\text{Li}$ and $\delta^{26}\text{Mg}$ in these waters (Figure 6), where clay formation should cause a negative covariation because clays tends to preferentially take up light Li but heavy Mg isotopes, shows that temperature-dependent stable isotope fractionation is not the controlling process for Mg isotopes.

Such a relationship could have interesting effects on the oceanic Mg isotope mass balance if the removal of Mg through hydrothermal interactions is not fully quantitative. Although



it is debated whether the modern oceans are in concentration or isotopic equilibrium for Mg (Holland, 2005; Tipper et al., 2006b; Pogge von Strandmann et al., 2014; Higgins and Schrag, 2015; Gothmann et al., 2017; Voigt et al., 2020), if we assume for simplicity's sake that they are, the mass balance can be inverted to determine the effect of isotope fractionation caused by a not fully quantitative Mg removal associated with the Rayleigh fractionation observed in our Myvatn samples. We use the original basic steady-state oceanic Mg mass balance of Tipper et al. (2006b):

$$\delta_{SW} = f_{riv}\delta_{riv} - [f_{dol}\Delta_{dol} + f_{hyd}\Delta_{hyd} + f_{hydet}\Delta_{hydet}]$$

where f is the fraction the source or sink flux for rivers, dolomite, hydrothermal, and the hypothetical “hydrothermal return,” which designates the efficiency of the hydrothermal sink, make up of the total source or sink. δ is the $\delta^{26}\text{Mg}$ of the source or of seawater (SW), and Δ is the isotopic fractionation imposed by the sinks. This is then solved for three separate individual parameters: (i) the dolomite $\Delta^{26}\text{Mg}$ [set to -1.7‰ when not varied (Pogge von Strandmann et al., 2014)], (ii) the riverine $\delta^{26}\text{Mg}$ [set to -1.09‰ when not varied (Tipper et al., 2006b)], and (iii) the amount of the total sink comprised by dolomite [set to 15% when not varied (Tipper et al., 2006b)]. For example, as summarized in **Figure 7**, to maintain a steady-state seawater $\delta^{26}\text{Mg}$ of -0.82‰ (Foster et al., 2010), if the hydrothermal sink efficiency for Mg is 90% (with a fractionation of -1.27‰ , as determined from the Myvatn Rayleigh relationship), then dolomite must cause a fractionation of -0.96‰ . In contrast, if that sink efficiency is 99.9%, then the dolomite fractionation must be -1.78‰ .

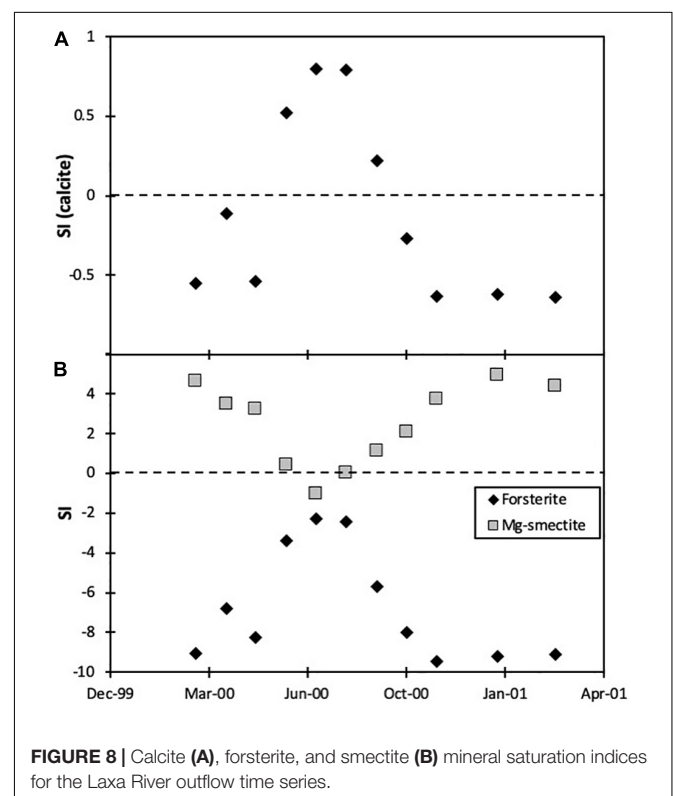
Equally, if the dolomite fractionation were constant, then the amount of Mg that dolomite removes from seawater would have to decrease with increasing hydrothermal removal efficiency. Finally, if both the dolomite sink and Mg isotope fractionation were constant, then the global riverine $\delta^{26}\text{Mg}$ would have to

change to maintain a constant seawater $\delta^{26}\text{Mg}$, as shown in **Figure 7**. In other words, different parameters of the global ocean Mg mass balance can be significantly affected by the efficiency of Mg removal by the hydrothermal sink if, as shown here, there is an isotopic fractionation associated with that sink.

Laxa River Outflow

Previous work on these outflow samples show that two phytoplankton blooms occurred during the year, the first during May–June and the second during August–September, representing the spring and autumn diatom blooms (Opfergelt et al., 2011). During these periods, NO_3^- concentrations are at a minimum, as nutrients are being scavenged for plankton growth. In general, the groundwater is thought to act as a constant source of dissolved nutrients, split between cold springs ($\sim 80\%$ of input) and hot springs ($\sim 20\%$). Thus, the phytoplankton blooms are controlled by the buildup of nutrients during the ice-covered season, and the spring bloom then occurs immediately after ice breakup. A second bloom then occurs in the autumn, corresponding to the second decline in dissolved nitrate (**Table 1**).

Silicon isotopes are strongly affected by these blooms: diatoms preferentially take up the light Si isotope, driving the lake water isotopically heavy. This results in Si isotopes showing a double peak during these periods. In contrast, Si concentrations only show a single minimum, with values declining throughout spring and increasing again after the July minimum (**Figures 8, 9**) (Opfergelt et al., 2011).



In contrast, lithium is an element largely unaffected by any biology, including phytoplankton. Li concentrations are unaffected by any of the phenomenon that affect other elements in these samples (Pogge von Strandmann et al., 2016). Equally, Li isotope ratios also exhibit broadly constant values throughout the year, showing that $\delta^7\text{Li}$ is unaffected by plankton growth (Figure 9). Li isotopes are normally strongly affected by secondary mineral formation (Hindshaw et al., 2019; Pogge von Strandmann et al., 2019a). PHREEQC calculations show that the saturation state of several minerals changes dramatically during the year. For example, olivine is strongly undersaturated during the winter but approaches saturation in summer (Figure 8). Equally, secondary minerals such as smectite are supersaturated during the winter but become undersaturated in the summer. It is, however, unclear how much this change represents actual changes in mineral saturation and how much is element utilization by plankton (misinterpreted by PHREEQC as changes in saturation). The invariant Li isotopes suggest that silicate secondary mineral formation does not change much during the year, implying that plankton, rather than mineral precipitation, are primarily changing elemental concentrations during the course of the year.

Mg isotopes do not exhibit a double peak like Si isotopes or NO_3 concentrations (Figure 9). Instead, they more closely follow trends like pH, which also only show a single maximum (Opfergelt et al., 2011). This implies that Mg isotopes are not being fractionated by the phytoplankton (of which diatoms make up approximately two-thirds), which is also suggested by the relatively unchanging Mg concentrations, which are clearly not limiting plankton growth. This presents a contrast to coccolith growth experiments, where the phytoplankton preferentially took up light Mg isotopes (Ra and Kitagawa, 2007). On the other hand, it has been suggested that plants have little overall effect on riverine Mg isotope ratios (Tipper et al., 2012b), although this effect does appear to depend on location and stream size (Pogge von Strandmann et al., 2019b). This may present a difference between laboratory growth experiments and natural samples, and of course, the diatoms that make up a large proportion of the Myvatn phytoplankton may also not fractionate Mg isotopes.

Equally, it does not seem that Mg isotopes are being controlled by the precipitation of silicate secondary minerals. If the PHREEQC saturation calculations are correct, maximum precipitation of minerals like Mg smectite should occur in the winter months (Figure 8). However, smectites, and most other secondary silicates, preferentially take up heavy Mg isotopes, driving residual waters isotopically light (Tipper et al., 2006a, 2008; Opfergelt et al., 2012; Pogge von Strandmann et al., 2012; Chapela Lara et al., 2017; Hindshaw et al., 2020). Thus, if precipitation of these minerals were controlling the Mg isotopes, it would be expected that, during winter, Mg isotope ratios would be lower than that of the initial basalt ($\sim -0.25\text{‰}$). Instead, during the winter, the outflow Mg isotope ratios are within analytical uncertainty of basalt, implying only dissolution with little secondary mineral formation.

However, a secondary mineral that is suggested by PHREEQC to be undersaturated during the winter and supersaturated during the summer is calcite. From June to September, calcite

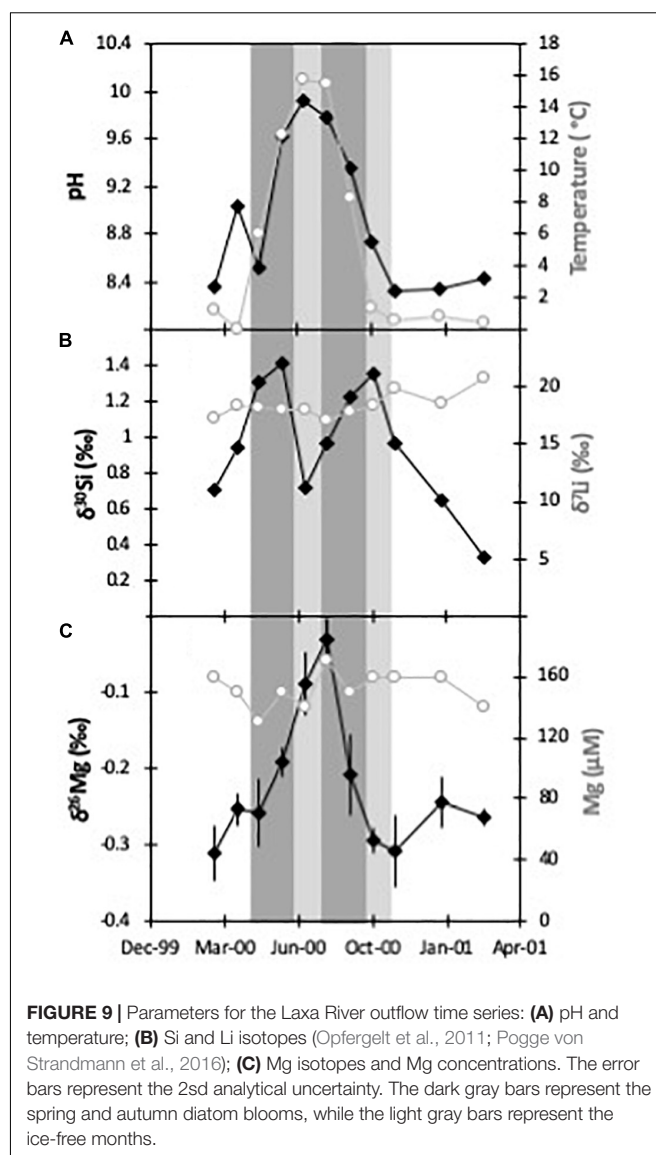
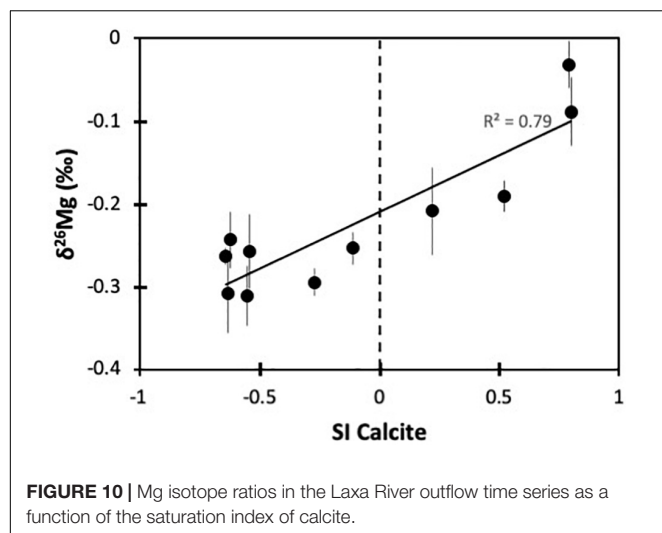


FIGURE 9 | Parameters for the Laxa River outflow time series: (A) pH and temperature; (B) Si and Li isotopes (Opfergelt et al., 2011; Pogge von Strandmann et al., 2016); (C) Mg isotopes and Mg concentrations. The error bars represent the 2sd analytical uncertainty. The dark gray bars represent the spring and autumn diatom blooms, while the light gray bars represent the ice-free months.

precipitates in Lake Myvatn, not only suggested by our saturation calculations but also confirmed by precipitation boxes placed on the bottom of the lake (Thorbergssdottir and Gislason, 2004). Calcite preferentially takes up light Mg isotopes, driving residual waters isotopically heavy (Immenhauser et al., 2010; Wombacher et al., 2011; Mavromatis et al., 2012; Saulnier et al., 2012; Saenger and Wang, 2014). The calcite saturation state corresponds to Mg isotopes in Lake Myvatn, where values are only distinguishable from primary basalt from June to September, when they become isotopically heavier. A calcitic control on Mg isotope ratios is also suggested by a direct positive covariation between the calcite SI and $\delta^{26}\text{Mg}$ ($r^2 = 0.79$; Figure 10).

Calcite precipitation has previously been observed driving riverine Mg isotope ratios heavy in Iceland during highly supersaturated outflow from the 2010 Eyjafjallajökull eruption (Pogge von Strandmann et al., 2019c). In this case, calcite SI reached values of > 1.5 , travertine precipitation was observed, and $\delta^{26}\text{Mg}$ changed by over 2.5‰ . Here at Myvatn, calcite never



becomes quite as supersaturated (maximum SI = 0.8), and $\delta^{26}\text{Mg}$ changes considerably less. This may also be exacerbated by the much larger water reservoir in Lake Myvatn and the Laxa River, compared to the smaller streams samples from Eyjafjallajökull.

Given that the groundwater influx rate into Lake Myvatn is fairly constant at 33 m³/s, it follows that the outflow rate through the Laxa River is broadly the same rate (Olafsson, 1979a; Opfergelt et al., 2011). Assuming that Mg isotopes are solely being fractionated by calcite formation, with a known fractionation factor of $\alpha = 0.9965$ (Mavromatis et al., 2013; Saenger and Wang, 2014; Pogge von Strandmann et al., 2019c), up to 8% of dissolved Mg is lost into calcite (Pogge von Strandmann et al., 2019c). Following the calculations detailed in Pogge von Strandmann et al. (2019c), using the Laxa outflow rate and the volume of Lake Myvatn ($\sim 9.25 \times 10^7$ m³), the calcite precipitation rate reaches a maximum of ~ 53 t/month (~ 6 mmol/month/m³) in August. Over the course of a year, this results in the precipitation of ~ 240 t/year calcite. However, during the winter months, calcite is undersaturated, and much of this calcite may redissolve, as also predicted elsewhere (Thorbergssdottir and Gislason, 2004). Overall, this calcite precipitation is an order of magnitude less than the Si sequestration by diatom growth of $\sim 7,500$ t/year (Opfergelt et al., 2011), showing that the phytoplankton (including diatoms) in Myvatn can have a significantly larger effect on the concentration of many elements compared to calcite precipitation. In comparison, the stream draining the Eyjafjallajökull eruption exhibited a Mg isotope-based calcite precipitation rate of 3,200 t/year (Pogge von Strandmann et al., 2019c).

The precipitation of that amount of calcite would sequester ~ 105 t/year of atmospheric CO₂, in lake-stored carbonate. Eventual dissolution of that calcite would release alkalinity, which the Laxa River would transport to the oceans, where it would form marine carbonate, again sequestering CO₂ on the timescale of the completion of the carbonate weathering reaction, which is on the order of a few 1000 years (Archer et al., 2000). Thus, even if the carbonate that forms within Lake Myvatn is redissolved, it still

acts as a medium-term CO₂ sink, meaning that, overall, the lake is a location of carbon sequestration even when not considering any potential burial of organic carbon.

CONCLUSION

This study analyzed Mg isotope ratios in hydrothermal and groundwaters of different temperatures that form the primary input into Lake Myvatn, Iceland. There is a clear trend between their $\delta^{26}\text{Mg}$ and temperature, such that $\delta^{26}\text{Mg}$ values decrease with increasing temperature. Hence, as Mg is removed, Mg isotopes become increasingly fractionated, with a fractionation factor of $\alpha \sim 1.00045$. Hydrothermal solutions are the main sink of Mg from modern seawater. While they are generally considered to be a quantitative sink (i.e., causing no isotope fractionation), if they are not fully efficient, our data suggest that they will cause significant fractionation, with consequences for the ocean mass balance.

This study also examined Mg isotopes from a time series of the Laxa River, the only outflow from Lake Myvatn. This lake is one of the most productive in the northern hemisphere and has a strong seasonal growth rate dependence that affects nutrients like NO₃ and Si. Mg isotopes do not exhibit the double peak typical of the two seasonal growth cycles but do exhibit a single peak, reaching maximum values in August. This behavior appears to correspond to the saturation behavior of calcite, which preferentially takes up light Mg isotopes driving residual water isotopically heavy. Hence, calcite is precipitated in the lake during summer and then likely dissolved again during winter when calcite is undersaturated, following which it will contribute alkalinity to the oceans. Myvatn is thus a CO₂ sink even without considering the formation and burial of its organic carbon.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/supplementary material.

AUTHOR CONTRIBUTIONS

PP analyzed the samples, interpreted the data, and wrote the manuscript. KB, SO, AE, EE, and SG provided samples and local knowledge. MM assisted with analyses. All co-authors assisted with interpretation.

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